Computational Scheme for the Step Growth Polymerization of Multifunctional Monomers in Presence of Intramolecular Reactions

INTRODUCTION

Several attempts have been made in the literature to determine the effect of intramolecular reactions, and these have been reviewed recently by Stepto.[1] There are three approaches taken in the literature to analyze the effect of intramolecular reactions on the step growth polymerization. The first one is based on expectation considerations,[2] in which the expectation of branching is computed. The second one is the cascade theory[3-5] in which the probability of the individual reactions are written. The last one is the kinetic approach which has been used to obtain the MWD and the point of gelation. The presence of intramolecular reactions shows the shift in the gel point, and all the theories proposed is to attempt to explain this shift.
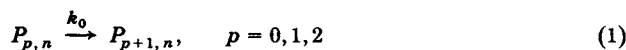
The kinetic approach has been used recently[6-18] to predict chain length distributions and the onset of gelation both for batch reactors[6,8,9] as well as for homogeneous continuous flow stirred tank reactors (HCSTRs).[10-15] The kinetic approach is particularly well suited for modelling nonlinear polymerizations in HCSTRs. In our earlier work[19] we presented the kinetic approach to get the MWD for batch reactors in presence of intramolecular reactions. To solve the MWD up to the gel point numerically is almost an impossible task because of the following reasons: To keep the truncation error minimal, it is important that the total number of species be continually increased with the conversion. As the gel point is approached, the total number of differential equations increase to about 1000. The time required to solve these is so large that the computation has to be done in several batches, and the total CPU time taken was close to 5 h on DEC 1090.

In this work we have developed an approximation that gives results to within 2% of the exact computation all the way up to the gel point. The CPU time taken is close to 20 min as opposed to 5 h for the exact computations. This way there is a considerable saving of computational time. The stage is now set to establish the effect of intramolecular reaction on the gel point using the kinetic approach.

KINETIC MODEL

We have aggregated molecular species into classes of n-mers and p-cyclic bonds and defined species $P_{p,n}$ as the one having chain length n with p intramolecular bonds. Due to steric hinderance, it is sometimes found that there is a minimum chain length n_p below which p intramolecular bonds on the polymer molecules cannot be formed. Assuming that the various reactions are irreversible, the polymerization can now be represented by[20]:

Intramolecular reaction:

$$P_{p,n} \xrightarrow{k_0} P_{p+1,n}, \qquad p = 0, 1, 2 \tag{1}$$

Polymer growth:

$$P_{p,m} + P_{q,n} \xrightarrow{k} P_{p+q,m+n} \tag{2}$$

k_0 is the rate constant for the formation of intramolecular bonds and k is the rate constant for polymerization.

For a given chain length n, the rate constant for the formation of intramolecular bonds between two functional groups separated by j repeat units has been found by Monte Carlo

studies to be given by

$$k_0(n, j) = k_0'(ej + g) \tag{3}$$

where k_0', e, and g are constants and depends upon the type of species. The average value for $k_0(n, j)$ is obtained by averaging over all j and is given by

$$\bar{k}_0(n) = \frac{1}{(n-1)} \int_l^n k_0'(ej + g)\, dj$$

$$= k_0'(1 \cdot n + m) \tag{4}$$

where l and m are other constants given as

$$l = e/2, \qquad m = e/2 + g \tag{5}$$

A molecule $P_{\nu, n}$ is formed either when $P_{p, r}$ ($p < \nu$ and $r < n$) reacts with $P_{\nu-p, n-r}$ for all possible values of p or when $P_{\nu-1, n}$ reacts intramolecularly. Similarly $P_{\nu, n}$ is depleted either when it reacts with any other molecule or when it reacts intramolecularly. If it is assumed that the maximum number of intramolecular bonds formed are ν_m, the mole balance for $P_{\nu, n}$ in batch reactors is given by

$$\frac{d[P_{\nu, n}]}{dt} = 2k_0(n)[P_{\nu-1, n}] - 2k(n)[P_{\nu, n}]$$

$$+ k \sum_{p=0}^{\nu} \sum_{r=1}^{n-1} \{ar - (\nu - p - 1)\}\{a(n-r) - (p-1)\}[P_{\nu-p, r}][P_{p, n-r}]$$

$$- 2k\{an - (\nu - 1)\}[P_{\nu, n}] \sum_{p=0}^{\nu_m - \nu} \sum_{m=n_p}^{\infty} [P_{p, m}]\{am - (p-1)\} \tag{6}$$

where

$$a = (f - 2)/2 \tag{7}$$

In eq. (7), f is the functionality of the monomer RA_f and n_p is the minimum chain length of the polymer molecules which can have p intramolecular bonds. ν_m is the maximum number of rings in the molecule.

THEORETICAL DEVELOPMENTS

Our earlier studies consisted of solving the MWD relations given in eq. (6) for all n and ν. To minimize the truncation error in computation, we define a repeat count variable RC given by

$$\text{RC} = \sum_{n=n_0}^{N_0} n \cdot [P_{0, n}] + \sum_{n=n_1}^{N_1} n[P_{1, n}] + \sum_{n=n_2}^{N_2} n[P_2, n] \tag{8}$$

where $N_0, N_1, N_2, \ldots, N_{\nu_m}$ are the total number of differential equations solved for each of the species. To keep RC equal to 1 within 2% error, N_0, N_1, etc. must be continuously increased. Among these, N_0 was found to increase most rapidly and takes on a value of 700 at conversions close to gel point.

Based on our previous work, we assume here that the concentrations of various oligomers of $P_{0, n}$ species are negligibly affected by the presence of intramolecular species. If there is no intramolecular reaction (i.e., $\nu_m = 0$), the MWD can be found analytically and is given by[21]

$$\frac{[P_{0, n}]}{[P_{01}]_0} = \frac{\{(f-1)n\}!}{n!\{n(f-2) + 2\}!} f(p_A)^{n-1}(1 - p_A)^{n(f-2)+2} \tag{9}$$

where p_A is the conversion of functional groups. It is observed that if p_A for $P_{0,n}$ species can be found then one can get the MWD of $P_{0,n}$ species by eq. (9) without solving the differential equations of $P_{0,n}$. This is done as follows.

We define the moments of the distribution of species $P_{\nu,n}$ as

$$\lambda_{\nu,i} = \sum_{n=1}^{\infty} n^i [P_{\nu,n}], \qquad i = 0, 1, 2 \tag{10}$$

where, in $\lambda_{\nu,i}$, i could take on values of 0, 1, and 2 for the zeroth, first, and second moments. The subscript ν has the usual meaning of the number of intramolecular rings on the species $P_{\nu,n}$. Since the total numbers of repeat units in the reaction mass is time-invariant, one has the following relation:

$$\sum_{\nu=0}^{\nu_m} \lambda_{\nu,1} = 1 \tag{11}$$

To determine p_A in eq. (9), it is necessary to determine λ_{00}, and this can be found from the mole balance equations of $P_{0,n}$. Equation (6) for $\nu = 0$ is

$$\frac{d[P_{0,n}]}{dt} = -2k_0(l \cdot n + m)[P_{0,n}] + k\left\{ \sum_{r=1}^{n-1} (ar + 1)\{a(n-r) + 1\}[P_{0,r}][P_{0,n-r}] \right\}$$

$$- 2k\{an + 1\}[P_{0,n}] \sum_{p=0}^{\nu_m} \sum_{m=1}^{\infty} (am + 1)[P_{p,m}] \tag{12}$$

If these MWD equations are added for all n, one has

$$\frac{d\lambda_{0,0}}{dt} = -2k_0' l \cdot \lambda_{0,l} - 2k_0 m \lambda_{0,0} - k(a\lambda_{0,1} + \lambda_{0,0})^2$$

$$- 2k(a\lambda_{0,1} + \lambda_{00})\alpha \tag{13}$$

where

$$\alpha = \sum_{p=1}^{\nu_m} \sum_{m=1}^{\infty} (am + 1 - p)[P_{pm}]$$

To determine p_A, it is observed that, on $P_{0,n}$, there are $2(n-1)$ reacted A groups and $(2an + 2)$ unreacted A groups. Therefore, the total number of reacted A groups can be obtained as

$$\text{total reacted A groups on } P_{0n} = \sum_{n=1}^{\infty} 2(n-1)[P_{0,n}]$$

$$= 2(\lambda_{0,1} - \lambda_{0,0}) \tag{14}$$

At any given time, a molecule of $P_{0,n}$ has n repeat units and therefore a total of (nf) functional groups. This implies that the total number of functional groups at any given time is given by

$$\text{total number of functional groups on } P_{0n} \text{ species}$$

$$= \sum_{n=1}^{\infty} fnP_{0n} = f\lambda_{0,1} \tag{15}$$

Therefore, p_A is given by

$$p_A = \frac{2(\lambda_{0,1} - \lambda_{0,0})}{f\lambda_{0,1}}$$ (16)

Major difficulty faced in obtaining a numerically stable solution is the choice of time increment Δt, specially near the gel point. We have found that Δt must be reduced as the conversion increases and we use the following set for consistent results:

$$\Delta t = 0.0004 \quad \text{up to 19\% conversion}$$

$$= 0.0002 \quad \text{between 19\% and 21\% conversion}$$ (17)

To demonstrate the efficiency of this algorithm of computation, we have chosen $f = 6$ and $n_0 = 1$, $n_1 = 4$, $n_2 = 6$, and $\nu_m = 2$. The final equations are given in Table II, and these have been written in the nondimensional form using the following variables:

$$p_{\nu,n} = \frac{[P_{\nu,n}]}{[P_{0,1}]_0}, \quad \nu = 0, 1, 2, \quad n = 1, 2, \ldots, \infty$$ (18a)

$$k_0 = k_0'/k$$ (18b)

$$x = k[P_{0,1}]_0 t$$ (18c)

where $[P_{0,1}]_0$ is the concentration of RA_f monomer charged initially to the batch reactor. The repeat count variable RC is given by

$$RC = \sum_{n=1}^{N_a} n[P_{0,n}] + \sum_{n=4}^{N_b} n[P_{1,n}] + \sum_{n=6}^{N_c} n[P_{2,n}]$$ (19)

We took $N_a = 30$, $N_b = 10$, $N_c = 10$ initially, but we made the computer program in such a way that they were incremented by 10 whenever the $N_a[P_{0,N_a}]$, $N_b[P_{1,N_b}]$, etc. increased beyond 10^{-6}.

ALGORITHM

The algorithm of computation can now be easily written and is given in Table I. It is assumed that the feed conditions are known. All the moments are first computed by using eq. (10) for the initial MWD. Since the total number of repeat units are time-invariant,

$$\lambda_{0,1} = 1 - \sum_{\nu=1}^{\nu_m} \lambda_{\nu 1}$$ (20)

Using the fourth order Runge–Kutta method, eq. (13) is solved for $\lambda_{0,0}$ by choosing sufficiently small Δt value (i.e., 0.0004), which is later modified according to eq. (17). The solution of eq. (16) gives p_A, and this is used for computing $[P_{0,n}]$ using eq. (9). The following recursive relation, for $f = 6$ is obtained from eq. (9) and is found to be the most convenient way of obtaining MWD of $P_{0,n}$ species. It is given as

$$P_{0,1} = (1 - p_A)^6 \lambda_{0,1}$$ (21)

$$P_{0,n+1} = \frac{5(5n+4)(5n+3)(5n+2)(5n+1)}{(4n+6)(4n+5)(4n+4)(4n+3)} p_A(1 - p_A)^4 \cdot P_{0,n}$$ (22)

TABLE I
Algorithm of Computation of the MWD of Various Species

Initial condition
Define $P_{\nu n}$; $\forall$ ν, n

t_{max}, N_a, N_b, N_c
$\downarrow$
Calculate $\lambda_{\nu n}$; $\forall$ ν, n
$\downarrow$
Solve eq. (13) for small Δt for λ_∞
(using fourth order Runge–Kutta method)
$\downarrow$
Calculate p_A by using eq. (16)
$\downarrow$
Calculate P_{01} by using eq. (21)
$\downarrow$
Calculate P_{0n}; for $n = 2, 3, \ldots, \infty$
[using eq. (22)]
$\downarrow$
Solve eq. (6) for $P_{\nu n}$ with $\nu = 1, 2, \cdots$
(use Table II)
Increment in no. of species by 10,
if $N_a[P_{0N_a}]$, $N_b[P_{1N_b}]$, or $N_c[P_{2N_c}]$
exceeds 10^{-6}
$\downarrow$
$t = t + \Delta t$
[Δt is chosen according to eq. (17)]
$\downarrow$

Yes

If
$t_{max} > t$

No
Out

The MWD's of species $P_{\nu n}$, other than $P_{0, n}$, are obtained by numerically integrating eq. (6). The values of $N_a[P_{0, N_a}]$, $N_b[P_{1, N_b}]$, and $N_c[P_{2, N_c}]$ are checked, and, whenever their values increase beyond 10^{-6}, N_a, N_b, and N_c are increased by 10. These steps are repeated till the final time of polymerization is reached.

RESULTS AND DISCUSSION

For the polymerization of hexafunctional monomers, various mole balance relations have been written in Table II. These have been solved using the exact and the approximate method outlined in this paper. The results on various moments and the molecular weight distributions have been compared in Table III and IV, respectively.

As already discussed in our earlier work, we have found that on taking $\nu_m + 2$, the self-poly-merization of hexafunctional monomers is adequately described. In Table III, we have given the first three moments of $P_{\nu n}$ species for $\nu = 0, 1, 2$ using the exact and approximate techniques. Results have been presented for various times of polymerization. We find that the deviations are large for short times (i.e., $t = 0.002$), but, as time increases, the deviation becomes smaller and smaller. The deviation for short times is found to be large because, then, the concentration of various species is small (of the order of 10^{-5}) but this falls within the machine accuracy (single precision vs. double precision) of the computer and the truncation error specified in the pro-gramme (i.e., $N_i[P_{\nu i}]$ to about 10^{-6}). However, for $t = 0.01$ and beyond, the total conversions of the functional groups by both techniques are almost identical. By the time the conversion increases up to 10% value, the numerical values of various moments also increase, and the deviations between the approximate and the exact techniques shrink to about 1%.

TABLE II
MWD Equations for Batch Reactors for the Case
of $\nu_m = 2$, $n_0 = 1$, $n_1 = 4$, $n_2 = 6$

MWD equation:

(A) For $n < 4$

$$\frac{d[P_{0,1}]}{dt} = -2k(a+1)[P_{0,1}]\left\{ \sum_{p=0}^{2} \sum_{m=1}^{\infty} \{am - (p-1)\}[P_{p,m}] \right\}$$

$$\frac{d[P_{0,n}]}{dt} = k \sum_{r=1}^{n-1} (ar+1)\{a(n-r)+1\}[P_{0,r}][P_{0,n-r}]$$

$$-2k(an+1)[P_{0,n}] \sum_{p=0}^{n-1} \sum_{m=1}^{\infty} \{am - (p-1)\}[P_{p,m}]$$

(B) For $4 \leq n < 6$

$$\frac{d[P_{0,n}]}{dt} = -k_0(n)[P_{0,n}] + k \sum_{r=1}^{n-1} (ar+1)\{a(n-r)+1\}[P_{0,r}][P_{0,n-r}]$$

$$-2k(an+1)[P_{0,n}] \sum_{p=0}^{2} \sum_{m=np}^{\infty} \{am - (p-1)\}[P_{pm}]$$

$$\frac{d[P_{1,n}]}{dt} = k_0(n)[P_{0,n}] - k_0(n)[P_{1n}] + k \sum_{p=0}^{1} \sum_{r=4}^{n-1} \{ar - (p-1)\}\{a(n-r)+p\}$$

$$\times [P_{pr}][P_{1-p,n-r}] - 2kan[P_{1,n}] \sum_{p=1}^{1} \sum_{m=np}^{\infty} \{an - (p-1)\}[P_{pm}]$$

(C) For $N \geq 6$

$$\frac{d[P_{0,n}]}{dt} = -k_0(n)[P_{0n}] + k \sum_{r=1}^{n-1} (ar+1)\{a(n-r)+1\}[P_{0r}][P_{0,n-r}]$$

$$-2k(an+1)[P_{0n}] \sum_{p=0}^{2} \sum_{m=np}^{\infty} \{am - (p-1)\}[P_{pm}]$$

$$\frac{d[P_{1,n}]}{dt} = k_0(n)[P_{0n}] - k_0(n)[P_{1,n}] + k \sum_{r=1}^{n-1} \sum_{p=0}^{1} \{ar - (p-1)\}\{a(n-r)+p\}[P_{pm}]$$

$$\times [P_{1-p,1-r}] - 2kan[P_{1,n}] \sum_{p=0}^{1} \sum_{m=n_p}^{\infty} \{am - (p-1)\}[P_{pm}]$$

$$\frac{d[P_{2,n}]}{dt} = k_0(n)[P_{1,n}] + k \sum_{p=0}^{2} \sum_{r=4}^{n-1} \{ar - (p-1)\}\{a(n-r)-(2-p-1)\}$$

$$\times [P_{pr}][P_{2-p,n-r}] - 2k(an-1)[P_{2,n}] \sum_{m=1}^{\infty} (am+1)[P_{0,m}]$$

where $a = 2$ (for $f = 6$)

TABLE III
Various Moments of the Distribution at Different Times
Using the Exact as Well as Approximate Method[a]

Moments	$t = 0.002$		$t = 0.01$		$t = 0.02$	
	Exact	Approximate	Exact	Approximate	Exact	Approximate
$\lambda_{0,0}$	0.982	0.985	0.912	0.915	0.830	0.833
$\lambda_{0,1}$	0.128×10^{-8}	0.284×10^{-9}	0.583×10^{-6}	0.464×10^{-6}	0.580×10^{-5}	0.614×10^{-5}
$\lambda_{0,2}$	0.190×10^{-15}	0.119×10^{-16}	0.552×10^{-11}	0.430×10^{-11}	0.506×10^{-9}	0.412×10^{-9}
$\lambda_{1,0}$	1.000	1.000	0.999	1.000	0.999	1.000
$\lambda_{1,1}$	0.523×10^{-8}	0.115×10^{-8}	0.251×10^{-5}	0.199×10^{-5}	0.319×10^{-4}	0.286×10^{-4}
$\lambda_{1,2}$	0.116×10^{-14}	0.720×10^{-16}	0.417×10^{-10}	0.274×10^{-10}	0.349×10^{-8}	0.281×10^{-8}
$\lambda_{2,0}$	1.036	1.020	1.204	1.190	1.473	1.460
$\lambda_{2,1}$	0.213×10^{-7}	0.466×10^{-8}	0.110×10^{-4}	0.087×10^{-4}	0.158×10^{-3}	0.140×10^{-3}
$\lambda_{2,2}$	0.707×10^{-14}	0.436×10^{-15}	0.271×10^{-9}	0.176×10^{-9}	0.247×10^{-7}	0.196×10^{-7}
Conversion	0.00597	0.00596	0.0291	0.0291	0.0566	0.0566

Moments	$t = 0.03$		$t = 0.04$		$t = 0.054$	
	Exact	Approximate	Exact	Approximate	Exact	Approximate
$\lambda_{0,0}$	0.752	0.755	0.678	0.681	0.581	0.583
$\lambda_{0,1}$	0.253×10^{-4}	0.237×10^{-4}	0.593×10^{-4}	0.568×10^{-4}	0.130×10^{-3}	0.127×10^{-3}
$\lambda_{0,2}$	0.528×10^{-8}	0.443×10^{-8}	0.235×10^{-7}	0.193×10^{-7}	0.910×10^{-7}	0.672×10^{-7}
$\lambda_{1,0}$	0.999	0.999	0.999	0.999	0.999	0.999
$\lambda_{1,1}$	0.133×10^{-3}	0.123×10^{-3}	0.358×10^{-3}	0.337×10^{-3}	0.104×10^{-2}	0.098×10^{-2}
$\lambda_{1,2}$	0.388×10^{-7}	0.319×10^{-7}	0.181×10^{-6}	0.144×10^{-6}	0.731×10^{-6}	0.518×10^{-6}
$\lambda_{2,0}$	1.843	1.827	2.382	2.361	3.748	3.713
$\lambda_{2,1}$	0.777×10^{-3}	0.705×10^{-3}	0.262×10^{-2}	0.237×10^{-2}	0.124×10^{-1}	0.109×10^{-1}
$\lambda_{2,2}$	0.295×10^{-6}	0.237×10^{-6}	0.144×10^{-5}	0.111×10^{-5}	0.607×10^{-5}	0.413×10^{-5}
Conversion	0.0825	0.0825	0.1071	0.1070	0.1394	0.1389

[a]For $k'_0 = 0.0025$, $l = 24.785$, $m = 0.085$.

TABLE IV
MWD of Various Species at Different Times Using the
Approximate and the Exact Computations[a]

t	$P_{0,10}$		$P_{1,10}$		$P_{2,10}$	
	Exact	Approximate	Exact	Approximate	Exact	Approximate
0.0020	0.415×10^{-12}	0.268×10^{-12}	0.708×10^{-16}	0.123×10^{-16}	0.630×10^{-20}	0.078×10^{-20}
0.0100	0.158×10^{-6}	0.157×10^{-6}	0.117×10^{-9}	0.086×10^{-9}	0.406×10^{-13}	0.280×10^{-13}
0.0200	0.184×10^{-4}	0.186×10^{-4}	0.321×10^{-7}	0.231×10^{-7}	0.232×10^{-10}	0.156×10^{-10}
0.0300	0.170×10^{-3}	0.172×10^{-3}	0.371×10^{-6}	0.340×10^{-6}	0.561×10^{-9}	0.357×10^{-9}
0.0400	0.568×10^{-3}	0.573×10^{-3}	0.162×10^{-5}	0.157×10^{-5}	0.388×10^{-8}	0.227×10^{-8}
0.05040	0.112×10^{-2}	0.112×10^{-2}	0.411×10^{-5}	0.406×10^{-5}	0.150×10^{-7}	0.075×10^{-7}
0.0540	0.129×10^{-2}	0.130×10^{-2}	0.514×10^{-5}	0.508×10^{-5}	0.216×10^{-7}	0.102×10^{-7}

[a]For $k_0 = 0.0025$, $l = 24.785$, $m = 0.085$.

In Table IV, we have given concentrations of $P_{\nu,10}$ for $\nu = 0$, 1, and 2. Whenever the concentration of species increases beyond 10^{-6}, the deviation between the exact and approximate computations outlined in this paper reduces to less than 1%. Once again the deviations between the two are attributed to machine accuracy and the truncation error specified in the computer program. To test our hypothesis, we reduced the truncation errors to 10^{-10} and carried out approximate as well as the exact computations on double precision. On doing this, it takes

considerable computer time and the advantage of the approximation is lost. In view of it, this line of approach was discarded. The main purpose of the analysis of multifunctional polymerization using the kinetic approach is to examine the effect of intramolecular reactions on the gel point. Since the gel point is governed by the weight average chained length μ_w, the precise knowledge of the MWDs, especially the species which are present in trace amounts, is not so important. We find that the various moments and the conversion of functional groups are predicted with very high accuracy by the approximate technique outlined here. In future publications we will therefore study the effect of intramolecular reaction on gel point using this approximate technique which we find to be extremely effective.

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